

Atty. Docket #: 1999/B-002

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE****INTERNATIONAL APPL. NO.:** PCT/EP00/03468 :**INTERNATIONAL FILING DATE:** -04/17/2000- :**APPLICANT:** THOMAS BECHTOLD ET AL :**SERIAL NO:** (To be assigned) :**ART UNIT:****FILED:** -HEREWITH- :**EXAMINER:****FOR:** "PREPARATION OF AQUEOUS ALKALINE  
SOLUTIONS  
OF REDUCED INDIGOID DYES" :**Commissioner for Patents  
Box PCT  
Washington, D.C. 20231****"Express Mail" No.:** ET284672180**Date:** -OCTOBER 25, 2001-

I hereby certify that this paper, along with any other paper or fee referred to in this paper as being transmitted herewith, is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, postage prepaid, on the date indicated above, addressed to the Commissioner for Patents, Washington, D.C. 20231.

-Carrie A. McPherson-  
(Typed or printed name of mailing paper or fee)

Carrie A. McPherson  
(Signature of person mailing paper)

**TRANSMITTAL OF APPLICATION PAPERS  
TO U.S. DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371  
(37 CFR 1.494 OR 1.495)**

This Transmittal Letter is based upon PTO Form 1390 (as revised in May, 1993).

The above-identified applicant(s) (jointly with their assignee) have filed an International Application under the P.C.T. and hereby submit(s) to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay.
4. ☒ A proper Demand for International Preliminary Examination (IPE) was made to the appropriate Authority (IPEA) within the time period required.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2)) --
  - a. ☒ is transmitted herewith (required when not transmitted by International Bureau).
  - b. ☐ has been transmitted by the International Bureau. See WIPO Publication WO.00/66663.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A (verified) translation of the International Application into the English language is enclosed.
7. ☐ Amendments to the (specification and) claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
  - e. ☐ will be submitted with the appropriate surcharge.
8. ☐ A translation of the amendments to the claims (and/or the specification) under PCT Article 19 (35 U.S.C. §371(c)(3)) is enclosed or will be submitted with the appropriate surcharge.

9. ☒ An oath or declaration/power of attorney of the inventor(s) (35 U.S.C. §371[c][4]) -is enclosed-.  
☐ and is attached to the translation of (or a copy of) the International Application.  
☐ and is attached to the substitute specification.

10. ☐ A translation of at least the Annexes to the IPE Report under PCT Article 36 (35 U.S.C. §371[c][5]) is enclosed.

Items 11. to 16. below concern other document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98 is enclosed.  
12. ☒ An Assignment for recording and a separate cover sheet in compliance with 37 CFR 3.28 and 3.31 -is enclosed-.  
13. ☒ A FIRST preliminary amendment is enclosed.  
A SECOND or SUBSEQUENT preliminary amendment is enclosed.  
14. ☐ A substitute specification (including claims, abstract, drawing) is enclosed.  
15. ☐ A change of power of attorney and/or address letter is enclosed.  
16. ☒ Other items of information:

- ☒ This application is being filed pursuant to 37 CFR 1.494(c) or 1.495(c), and any missing parts will be filed before expiration of--

☐ 22 months from the priority date under 37 CFR 1.494(c), or

☒ 32 months from the priority date under 37 CFR 1.495(c).

- ☐ The undersigned attorney is authorized by the International applicant and by the inventors to enter the National Phase pursuant to 37 CFR 1.494(c) or 1.495(c).

The following additional information relates to the International Application:

International Application No. PCT/EP00/03468

1999/B-002

- ☒ Receiving Office: EPO
- ☒ IPEA (if filing under 37 CFR 1.495): EPO
- ☒ Priority Claim(s) (35 USC §§ 119, 365):  
German Appln. 199 19 746.6 filed -April 29, 1999-.
- ☒ A copy of the International Search Report is
- ☐ enclosed.
- ☒ attached to the copy of the International Application.
- ☒ A copy of the Receiving Office Request Form is enclosed.
- ☒ Form PTO/SB/05 (1) sheet
- ☒ Form PCT/IPEA/416 & 409 (In German) (8) sheets

The fee calculation is set forth on the next page of this Transmittal Letter.

## FEE CALCULATION SHEET

☒ A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 890.00

Total Number of claims in  
excess of (20) times \$18..... -0-

Number of independent claims  
in excess of (3) times \$ 84..... -0-

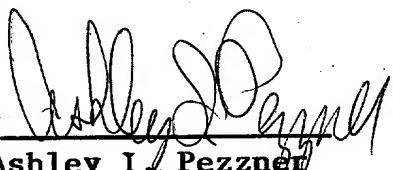
Fee for multiple dependent  
claims \$280..... -0-

TOTAL FILING FEE... \$ 890.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By 

Ashley I. Pezzner  
Reg. No. 35,646  
CONNOLLY BOVE LODGE & HUTZ LLP  
1220 Market Street  
P.O. Box 2207  
Wilmington, Delaware 19899  
Tel. (302) 658-9141

AIP/cam (5579\*281)

Enclosures

F:\docs\fori\40975 = F:\docs\patn\56657.doc

# FEE CALCULATION SHEET

☒ A check in payment of the filing fee, calculated as follows, is attached (37 CFR 1.492).

Basic Fee..... \$ 890.00

Total Number of claims in  
excess of (20) times \$18..... -0-

Number of independent claims  
in excess of (3) times \$ 84..... -0-

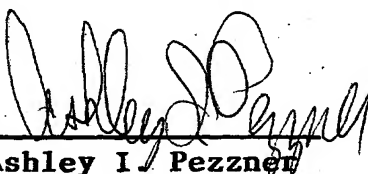
Fee for multiple dependent  
claims \$280..... -0-

TOTAL FILING FEE... \$ 890.00

Kindly send us the official filing receipt.

The Commissioner is hereby authorized to charge any additional fees which may be required or to credit any overpayment to Deposit Account No. 03-2775. This is a "general authorization" under 37 CFR 1.25(b), except that no automatic debit of the issue upon allowance is authorized. An additional copy of this page is attached.

Respectfully submitted,

By 

Ashley I. Pezzner  
Reg. No. 35,646  
CONNOLLY BOVE LODGE & HUTZ LLP.  
1220 Market Street  
P.O. Box 2207  
Wilmington, Delaware 19899  
Tel. (302) 658-9141

AIP/cam (5579\*281)

Enclosures

F:\docs\fori\40975 = F:\docs\patn\56657.doc

Please type a plus sign (+) inside this box → ☐

PTO/SB/05 (4/98)  
Approved for use through 09/30/2000. OMB 0651-0032  
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE  
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

# UTILITY PATENT APPLICATION TRANSMITTAL

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

Attorney Docket No. 1999/B-002  
First Inventor or Application Identifier THOMAS BECHTOLD ET AL  
Title PREPARATION OF AQUEOUS ALKALINE  
Express Mail Label No. ET284672180

## APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

Commissioner for Patents  
ADDRESS TO: Box Patent Application  
Washington, DC 20231

1. ☒ \* Fee Transmittal Form (e.g., PTO/SB/17)  
(Submit an original and a duplicate for fee processing)
2. ☒ Specification [Total Pages 08]  
(preferred arrangement set forth below)  
- Descriptive title of the Invention  
- Cross References to Related Applications  
- Statement Regarding Fed sponsored R & D  
- Reference to Microfiche Appendix  
- Background of the Invention  
- Brief Summary of the Invention  
- Brief Description of the Drawings (if filed)  
- Detailed Description  
- Claim(s)  
- Abstract of the Disclosure
3. ☐ Drawing(s) (35 U.S.C. 113) [Total Sheets 0]
4. Oath or Declaration [Total Pages 3]  
a. ☒ Newly executed (original or copy)  
b. ☐ Copy from a prior application (37 C.F.R. § 1.63(d))  
(for continuation/divisional with Box 16 completed)  
c. ☐ DELETION OF INVENTOR(S)  
Signed statement attached deleting  
inventor(s) named in the prior application,  
see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

5. ☐ Microfiche Computer Program (Appendix)
6. Nucleotide and/or Amino Acid Sequence Submission  
(if applicable, all necessary)  
a. ☐ Computer Readable Copy  
b. ☐ Paper Copy (identical to computer copy)  
c. ☐ Statement verifying identity of above copies

## ACCOMPANYING APPLICATION PARTS

7. ☒ Assignment Papers (cover sheet & document(s))
8. ☒ 37 C.F.R. § 3.73(b) Statement (when there is an assignee) ☒ Power of Attorney
9. ☒ English Translation Document (if applicable)
10. ☒ Information Disclosure Statement (IDS)/PTO-1449 ☒ Copies of IDS Citations
11. ☒ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503)  
(Should be specifically itemized)
13. ☐ \* Small Entity Statement(s) ☐ Statement filed in prior application, Status still proper and desired (PTO/SB/09-12)
14. ☐ Certified Copy of Priority Document(s)  
(if foreign priority is claimed)
15. ☒ Other: Rec. Office Request Form  
(9) pages in German  
16 X Form PCT/IPEA/416 & 409  
(8) pages in German

16. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No: \_\_\_\_\_

Prior application information: Examiner \_\_\_\_\_

Group / Art Unit: \_\_\_\_\_

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

## 17. CORRESPONDENCE ADDRESS

☐ Customer Number or Bar Code Label

or ☒ Correspondence address below

(Insert Customer No. or Attach bar code label here)

Name Ashley I. Pezzner, Esquire  
CONNOLLY BOVE LODGE & HUTZ LLP  
Address 1220 Market Street  
P.O. Box 2207  
City Wilmington State DE Zip Code 19899  
Country US Telephone (302) 888-6270 Fax (302) 656-9072

Name (Print/Type) ASHLEY I. PEZZNER Registration No. (Attorney/Agent) 35,646  
Signature [Signature] Date 10/24/01

Burden Hour Statement: This form is estimated to take 0.2 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Box Patent Application, Washington, DC 20231.

ATTORNEY DOCKET NO.: 1999/B 002 (5579\*281)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: THOMAS BECHTOLD *ET AL.* )  
SERIAL NO. TO BE ASSIGNED ) ART UNIT: TO BE ASSIGNED  
FILED: HEREWITH ) EXAMINER: TO BE ASSIGNED  
FOR: PREPARATION OF AQUEOUS )  
ALKALINE SOLUTIONS OF )  
REDUCED INDIGOID DYES )

Asst. Commissioner for Patents  
Washington, D.C. 20231

"EXPRESS MAIL" No. ET284672180 DATE: OCTOBER 25, 2001

I HEREBY CERTIFY THAT THIS PAPER OR FEE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE "EXPRESS MAIL POST OFFICE TO ADDRESSEE" SERVICE UNDER 37 CFR 1.10 ON THE DATE INDICATED AND IS ADDRESSED TO THE ASSISTANT COMMISSIONER FOR PATENTS, WASHINGTON, D.C. 20231

CARRIE A. MCPHERSON  
(TYPED OR PRINTED NAME OF  
PERSON MAILING PAPER OR FEE)

*Carrie A. McPherson*  
(SIGNATURE OF PERSON MAILING  
PAPER OR FEE)

PRELIMINARY AMENDMENT

Sir:

Prior to fee calculation and examination please amend the above-identified application as follows.

In the Claims

Please cancel claims 3-8.

Please add the following new claims

- -9. The process as claimed in claim 1, wherein from 0.003 to 0.08 mol of mediator is used per mole of dye.



10. The process as claimed in claim 1, wherein the dye to be reduced is not precharged all at once, but is added a little at a time.
11. The process as claimed in claim 1, wherein the alkali used is a mixture of at least two alkali metal hydroxides wherein none of the alkali metal hydroxides accounts for more than 70 mol%.
12. The process as claimed in claim 1, wherein from 1.2 to 2 mol of alkali are used per mole of dye.
13. The process as claimed in claim 1, wherein said reducing is effected at from 10 to 80°C.
14. The process as claimed in claim 1, wherein the solution prepared is a solution from 15 to 45% strength by weight leuco indigo solution.
15. The process as claimed in claim 2, wherein from 0.003 to 0.08 mol of mediator is used per mole of dye.
16. The process as claimed in claim 15, wherein the alkali used is a mixture of at least two alkali metal hydroxides wherein none of the alkali metal hydroxides accounts for more than 70 mol%.
17. The process as claimed in claim 16, wherein from 1.2 to 2 mol of alkali are used per mole of dye and said reducing is effected at from 10 to 80°C.
18. The process as claimed in claim 17, wherein from 0.008 to 0.05 mol of mediator is used per mole of dye. - -

REMARKS

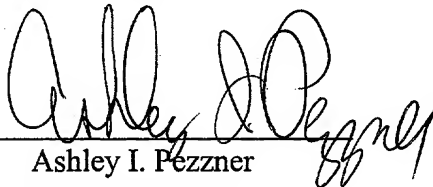
The applicants respectfully request that the preliminary amendment be entered prior to fee calculation and examination. The applicants have rewritten claims 3-8 in the proper U.S. form as newly added claims 9-14. Support for newly added claims 15-17 can be found in original claims 3, 5, 6 and 7. Support for newly added claim 18 can be found in the specification at the bottom of page 3.

No additional fee is required for the extra claims. If there are any additional fees due in connection with the filing of this response, including any fees required for an additional extension of time under 37 CFR 1.136, such an extension is requested and the Commissioner is authorized to charge or credit any overpayment to Deposit Account No. 03-2775.

A prompt and favorable action is solicited.

Respectfully submitted,

CONNOLLY BOVE LODGE & HUTZ LLP

By   
Ashley I. Pezzner  
Reg. No. 35,646  
Tel. (302) 888-6270

AIP/cam  
::ODMA\MHODMA\CB;163605;1

PREPARATION  
OF  
AQUEOUS ALKALINE  
SOLUTIONS  
OF  
REDUCED INDIGOID DYES

Thomas Bechtold  
Rudolf Krüger  
Peter Maier  
Georg Schnitzer  
Franz Sütsch  
Wolfgang Schrott  
-and-  
Norbert Grund

ENGLISH TRANSLATION  
OF  
INTERNATIONAL APPLICATION

PCT/EP00/03468

.... IFD: -April 17, 2000-

DYS 1999/B-002

.... (5579\*281)

"Express Mail" mailing label  
number ET284672180  
Date of Deposit  
-OCTOBER 25, 2001-  
I hereby certify that this paper or fee is  
being deposited with the United States Postal  
Service "Express Mail Post Office to  
Addressee" service under 37CFR 1.10 on the  
date indicated above and is addressed to Box  
PCT, Commissioner for Patents,  
Washington, D.C. 20231  
-Carrie A. McPherson-  
(Typed or printed name of person mailing  
paper or fee)  
Carrie A. McPherson  
(Signature of person mailing paper or fee)

Preparation of aqueous alkaline solutions of reduced indigoid dyes

#### Description

The present invention relates to a process for preparing from 5 to 60% strength by weight aqueous alkaline solutions of reduced indigoid dyes.

Indigoid dyes, especially indigo itself and its bromine derivatives such as Brilliant Indigo, are well known vat dyes, which are used for dyeing cellulosic textile material. Indigo is particularly important for dyeing cotton warp yarns for blue denim articles.

For dyeing, the water-insoluble dye first has to be reduced (vatted) to convert it into the water-soluble leuco form which has affinity for fiber and which, after going onto the material to be dyed, is then oxidized back to the water-insoluble vat dye pigment.

In conventional indigo dyeing processes, the indigo is reduced in a vessel upstream of the dyebath in an alkaline medium by using sodium dithionite (hydrosulfite) as reducing agent. This method usually produces 8% strength by weight leuco indigo solutions, and the dyehouse wastewater contains large amounts of sulfate and sulfite.

To avoid these disadvantages, a dyeing process was developed to utilize leuco indigo produced by catalytic hydrogenation (WO-A-94/23114). As described in prior German Patent Application 198 31 291.1, catalytic hydrogenation in conjunction with certain process measures can be used to produce leuco indigo solutions having a leuco indigo content of up to 55% by weight.

WO-A-90/15182, 95/07374 and 96/32445 disclose the electrochemical reduction of indigo in the presence of large amounts of a mediator (around 4.5 % by weight of iron, based on the indigo quantity) in very dilute solution (up to 0.5% strength by weight).

It is an object of the present invention to provide more concentrated indigoid dye solutions which are advantageously useful for dyeing.

We have found that this object is achieved by a process for preparing a from 5 to 60% by weight aqueous alkaline solution of

10/049728

a reduced indigoid dye, which comprises reducing said indigoid dye electrochemically in the presence of a mediator.

The mediator can be any redox system known for electrochemical dye reduction.

Examples are mediators based on quinonoid compounds such as anthraquinonesulfonic acids and hydroxyanthraquinones, e.g., 1,2-dihydroxy-9,10-antraquinone, and on quinoneimines and diimines and also mediators based on transition metal complex salts.

Among transition metal complex salts, iron(II/III) complex salts are particularly important.

Examples of particularly suitable complexing agents are triethanolamine, triisopropanolamine and bicine and the aliphatic hydroxy compounds described in DE-A-43 20 867, which contain at least two coordination-capable hydroxyl groups and may additionally contain up to two aldehyde, keto and/or carboxyl groups, in which connection compounds derived from sugars are of particular interest. Specifically, the following examples are preferred:

- di- and polyalcohols such as ethylene glycol, diethylene glycol, pentaerythritol, 2,5-dihydroxy-1,4-dioxane, especially sugar alcohols such as glycerol, erythritol, hexitols such as mannitol, dulcitol, sorbitol and galactitol;
- di- and polyhydroxyaldehydes such as glyceraldehyde, triose reductone, especially sugars (aldoses) such as mannose, galactose and glucose;
- di- and polyhydroxyketones such as, in particular, sugars (ketoses) such as fructose;
- di- and polysaccharides such as sucrose, maltose, lactose, cellubiose and molasses;
- di- and polyhydroxymonocarboxylic acids such as glyceric acid, particularly acids derived from sugars, such as gluconic acid, heptagluconic acid, galactonic acid and ascorbic acid;
- di- and polyhydroxydicarboxylic acids such as malic acid, particularly sugar acids such as glucaric acids, mannaric acids and galactaric acid;

- trihydroxycarboxylic acid such as citric acid.

It will be appreciated that mixtures of complexing agents can also be used.

Particular preference is given to monocarboxylic acids derived from sugars (especially gluconic acid and particularly heptagluconic acid) and their esters, lactones and salts.

The molar ratio between complexing agent and iron cation is customarily in the range from 15 : 1 to 5 : 1 in the case of iron(II/III)/triethanolamine complexes and generally in the range from 3 : 1 to 0.5 : 1, especially in the range from 1.5 : 1 to 0.5 : 1, in the case of complexes with the complexing agents described in DE-A-43 20 867, especially heptagluconic acid.

Iron(II/III) complex salts can be prepared by mixing iron(II) or (III) salts such as iron sulfate, iron acetate or preferably iron chloride with the complexing agent or one of its salts in the presence of water. The starting compounds can be used in the form of a solid or in the form of an aqueous solution. If an iron(III) salt is used, the iron(III) is preferably reduced to the active iron(II) complex at the start of the electrolysis.

The mediator is preferably used in the process of the invention in the form of an alkaline solution from about 5 to 8% strength by weight.

Surprisingly, the process of the invention needs a significantly smaller amount of mediator to reduce the indigoid dye than the above-described processes for electrochemical dye reduction. For instance, the amount used in the case of a mediator which transfers one electron per molecule is customarily in the range from 0.003 to 0.08 mol, preferably in the range from 0.008 to 0.05 mol, of mediator per mole of dye.

This small amount of mediator has little if any effect on the solubility of the reduced dye. Therefore, the mediator does not have to be removed from the ready-prepared leuco dye solution.

Advantageously, in the process of the invention, only a portion of the total amount of dye to be reduced is precharged to the electrolysis cell and the remainder is added a little at a time (in power or paste form) during the reduction. However, the addition of dye need not be commenced until after the current has been switched on. This makes it possible to produce even highly concentrated leuco dye solutions (especially > 20% strength by

weight leuco indigo solutions) without problems, which is not possible with reducing agents such as hydrosulfite or by hydrogenation.

It is particularly advantageous for viscosity reasons for the concentration of unvatte dye in the electrolysis bath not to exceed 25% by weight, especially 20% by weight.

If cathodes of carbon or graphite felt are used (and they permit a particularly high current yield), it is advisable to further lower the solids content of the electrolysis bath (and keep it as low as possible) so as to prevent blinding of or mechanical damage to the electrode material.

The reduced dye is soluble in an aqueous alkaline medium in the form of a leuco salt. Up to 20% by weight leuco indigo solutions are stable in the presence of one alkali metal hydroxide as alkali. At up to 80°C this is true for up to 40% by weight solutions.

To keep the reduced dye in stable solution at relatively high concentration (generally > 20% by weight) even at room temperature, it is advisable to convert the reduced dye into a mixed alkali metal salt. Accordingly, the alkali used for more concentrated solutions is preferably a mixture of at least two alkali metal hydroxides wherein none of the alkali metal hydroxides accounts for more than 70 mol%.

Preferred alkali metal hydroxides are lithium hydroxide, sodium hydroxide and potassium hydroxide, which may all be present as a triple mixture or in the form of the respective double combinations, in which case mixtures of sodium hydroxide and potassium hydroxide are particularly preferred.

In mixtures of two alkali metal hydroxides, the molar ratio between the two is preferably in the range from 2 : 1 to 1 : 2, particularly preferably in the range from 1.5 : 1 to 1 : 1.5, most preferably about 1 : 1.

It is further advisable to minimize the electrolyte excess in order that any salting out of the dissolved leuco dye may be prevented.

The alkali, especially the alkali metal hydroxide mixture, is therefore generally used in amounts of from 1.2 to 2 mol, preferably of from 1.4 to 1.8 mol, in particular of around 1.5

mol, per mole of leuco dye.

The process of the invention is customarily carried out at from 10 to 80°C. Higher temperatures >40°C increase not only the rate of reduction but also the solubility of the reduced dye. Thus the use of alkali metal hydroxide mixture and avoidance of an electrolyte excess will produce at about 40 - 60°C from 50 to 55% strength by weight and at 60 - 80°C from 55 to 60% strength by weight leuco indigo solutions devoid of any tendency to crystallize out.

The process of the invention may be carried out using the electrolysis cells disclosed in WO-A-90/15182, 95/07374 and 96/32445.

The process of the invention is useful for producing concentrated leuco salt solutions of all indigoid dyes, for example of indigo itself, mono-, di-, tri and tetrabromo- and/or -chloro-indigo and thioindigo and its derivatives.

The process of the invention is preferably used for producing from 15 to 45% strength by weight leuco dye solutions, in particular from 20 to 30% strength by weight leuco dye solutions, the corresponding leuco indigo solutions being of particular interest.

The leuco dye solutions obtained according to the invention are advantageously useful in indigo dyeing installations for all dyeing processes, for example yarn dyeing, exhaust dyeing, garment dyeing.

#### Example

A 20% strength by weight solution of reduced indigo was prepared using the electrolysis cell described in WO-A-96/32445, which is divided by a Nafion® membrane and has an anode and a cathode cycle. The anode (200 mm x 100 mm x 3 mm, planar surface area 2 dm<sup>2</sup>) consisted of RA<sub>4</sub> 1.457 (stainless steel). The cathode (identical dimensions) consisted of a carbon felt. An Ag/AgCl reference electrode was installed to be able to measure the cathode potential by means of a voltmeter. The potential was measured in solution via a Pt measuring electrode.

The following components were used to prepare 1 l of mediator solution:

53.6 g (0.33 mol) of iron(III) chloride



89 g (0.36 mol) of sodium heptagluconate  
786 g (786 ml) of distilled water  
53 g (35 ml) of 50% strength by weight sodium hydroxide solution  
73 g (49 ml) of 50% strength by weight potassium hydroxide

The following procedure was adopted: Iron(III) chloride and sodium heptagluconate were stirred into water. Sufficient alkali had been added during the dissolving of the salts for the pH of the solution to be maintained in the range from 3 to 5. On complete solution the remaining alkali was added a little at a time. The pH of the ready-prepared solution was 10.6.

The reduction was carried out by introducing into both the cathode space and the anode space of the electrolysis cell

924 ml of distilled water  
50 ml of the mediator solution  
90 ml of 50% strength by weight sodium hydroxide solution  
126 ml of 50% strength by weight potassium hydroxide solution

Additionally 4.3 g of indigo powder were introduced into the cathode space every 10 min for a period of 11 h 40 min at a constant electrolysis current of 6 A.

Following reduction of the indigo, the voltmeter indicated a potential of -850 mV.

1.5 kg were obtained of a 20% strength by weight aqueous leuco indigo solution having a density of 1.12 g/ml. The current yield was 88%.

We claim:

1. A process for preparing a from 5 to 60% by weight aqueous alkaline solution of a reduced indigoid dye, which comprises reducing said indigoid dye electrochemically in the presence of a mediator.
2. A process as claimed in claim 1, wherein said mediator is an iron(II/III) complex salt.
3. A process as claimed in claim 1 or 2, wherein, based on a mediator which transfers one electron per molecule, from 0.003 to 0.08 mol of mediator is used per mole of dye.
4. A process as claimed in any of claims 1 to 3, wherein the dye to be reduced is not precharged all at once, but is added a little at a time.
5. A process as claimed in any of claims 1 to 4, wherein the alkali used is a mixture of at least two alkali metal hydroxides wherein none of the alkali metal hydroxides accounts for more than 70 mol%.
6. A process as claimed in any of claims 1 to 5, wherein from 1.2 to 2 mol of alkali are used per mole of dye.
7. A process as claimed in any of claims 1 to 6, wherein said reducing is effected at from 10 to 80°C.
8. A process as claimed in any of claims 1 to 7 for preparing a from 15 to 45% strength by weight leuco indigo solution.

Preparation of aqueous alkaline solutions of reduced indigoid dyes

Abstract

From 5 to 60% by weight aqueous alkaline solutions of reduced indigoid dyes are prepared by reducing the indigoid dye electrochemically in the presence of a mediator.

1004929 102504

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

the specification of which is attached herewith

X was filed on April 17<sup>th</sup>, 2000 as Application Serial No. PCT/EP00/03468

was amended on

(if applicable)

was amended through

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, U S C, §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Claimed:

Federal Republic of Germany, 19919746.6

of April 29<sup>th</sup>, 1999

105201 322000

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

(filing date)

by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

(Status)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

[illegible]

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application, and transact all business in the Patent and Trademark Office connected therewith:

18  
In the matter of the above-identified application, please recognize Rudolf E. Hutz, Reg. No. 22,397; John Fairchild, Reg. No. 19,756; Harold Pezzner, Reg. No. 22,112; Richard M. Beck, Reg. No. 22,580; Paul E. Crawford, Reg. No. 24,397; Patricia Smink Rogowski, Reg. No. 33,791; Robert G. McMorrow, Jr., Reg. No. 30,962; Ashley I. Pezzner, Reg. No. 35,646; William E. McShane, Reg. 32,707; Mary W. Bourke, Reg. No. 30,982; Gerard M. O'Rourke, Reg. No. 39,794; James M. Olsen, Reg. No. 40,408; Francis DiGiovanni, Reg. No. 37,310; Eric J. Evain, Reg. No. 42,517; Daniel C. Mulveny, Reg. No. 45,897; Christine M. Hansen, Reg. No. 40,634; Patrick H. Higgins, Reg. 39,709 and Elliot C. Mendelson (Agent), Reg. No. 42,878, all of P.O. Box 2207, Wilmington, Delaware 19899-2007 as attorneys with full power of substitution to prosecute this application and conduct all business in the Patent and Trademark Office connected therewith.

Please send correspondence to:

Connolly Bove Lodge & Hutz LLP  
P.O. Box 2207  
Wilmington, Delaware 19899-2007

Direct Telephone Calls To:  
(302) 658-9141

1<sup>st</sup> Inventor

Prof. Dr. Thomas Bechtold

Dr. Thomas Bechtold  
Signature

06.08.01  
Date

Angelika Kaufmannstraße 4, 6850 Dornbirn, Austria

Citizenship: German

2<sup>nd</sup> Inventor

Dr. Rudolf Krüger

Dr. Rudolf Krüger 26.07.01  
Signature Date


Südtiroler Ring 5, 67273 Weisenheim, Germany

Citizenship: German

DYS 1999/B 002


3<sup>rd</sup> Inventor

30 Hans-Peter Maier

Signature 

Date

25.07.01

Reinsburgstraße 79, 70197 Stuttgart, Germany 

Citizenship: German


4<sup>th</sup> Inventor

40 Georg Schnitzer

Signature 

Date

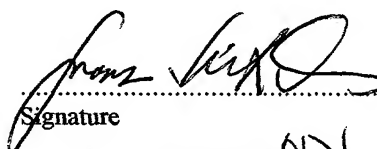
25-07-01

Ostendstraße 159c, 90482 Nürnberg, Germany 

Citizenship: German

5<sup>th</sup> Inventor

50 Franz Sütisch

Signature 

Date

25.07.01

Hauptstraße 159, 67127 Rödersheim-Gronau, Germany 

Citizenship: German

6<sup>th</sup> Inventor

60 Dr. Wolfgang Schrott

Signature 

Date

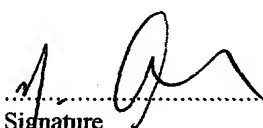
25.07.2001

Im Haingarten 6, 67459 Böhl-Iggelheim, Germany 

Citizenship: German


7<sup>th</sup> Inventor

70 Dr. Norbert Grund

Signature 

Date

25.07.2001

Merziger Straße 7b, 67063 Ludwigshafen, Germany 

Citizenship: German

Post Office Address of the Inventor(s):

DyStar Textilfarben GmbH & Co. Deutschland KG

Patent- und Lizenzabteilung

Werk Höchst - Geb. D 706

D-65926 Frankfurt am Main, Germany